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High catalytic activity of palladium nanoparticle clusters supported on a spherical polymer network†

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In this communication we report the synthesis of Pd nanoparticle clusters achieved *via* the assembly of Pd nanoparticles on the surface of a spherical polymer network. The network exhibits flexibility and adapts to the cluster formation. The nanoclusters display high catalytic activity toward *p*-nitrophenol reduction and the Suzuki–Miyaura coupling reaction.

Recently, metal nanoparticles (MNPs) have attracted much attention due to their unique properties that can find applications in various areas such as catalysis.[1–3] Latest developments have demonstrated that MNPs of size less than 8 nm and grouped into the nanoparticle clusters are the most attractive materials for the process of catalysis.[4–6] The assembly of MNPs into clusters reduces the size of the catalyst; the metal surface of the MNP clusters is uncapped with a stabilizer and, for this reason, they are more catalytically active. The interactions between the MNPs and between the MNPs and the supporting matrices in the clusters enhance the properties of the metals.[7–10]

Macrocyclic compounds have contributed to the progress in the synthesis of MNPs and their composites.[11,12] They were applied as reducing agents, stabilizers as well as supporting matrices, controlling the shape and size of the MNPs. Furthermore, macrocycles have a significant effect on the properties of nanoparticles and their controlled behavior. MNPs modified with macrocycles were applied in SERS spectroscopy, and in colorimetric sensing, as electrochemical sensors and catalysts.[11–14] In our previous paper we showed that Pd NPs can be obtained by electrochemical reduction of $[PdCl_4]^{2-}$ with an amphiphilic viologen-cavitand ($MVCA^{8+} \cdot 8Cl^-$) as a mediator.[15] $MVCA^{8+}$ effectively binds to $[PdCl_4]^{2-}$ *via* electrostatic interactions,

while the viologen groups of $MVCA^{8+}$ facilitate the reduction of $[PdCl_4]^{2-}$ to 0.6 V on a glassy carbon electrode. However, the Pd NPs formed are unstable in a solution and agglomerate in bulk. To enhance their stability, we have chosen a polymeric porous hollow shell as a supporting matrix. The shell consists of viologen-cavitands which are covalently linked by styrene and form a flexible spherical network (*p*(MVCA-*co*-St), Scheme 1).[16] *p*(MVCA-*co*-St) is highly soluble in water. Viologen groups located on the surface are able to stabilize the MNPs, enhancing their catalytic activity.[17,18] We assumed that the MNPs on *p*(MVCA-*co*-St) could be assembled into a cluster due to the flexible, mobile and tunable shape of *p*(MVCA-*co*-St), capable of adapting to the MNP cluster structure. Herein, we report the synthesis and structural investigation of Pd NP clusters with *p*(MVCA-*co*-St) as the supporting matrix. The catalytic properties of the clusters in the reduction reaction of *p*-nitrophenol[19–21] and the Suzuki–Miyaura coupling reaction are discussed.[22,23]

For the synthesis of Pd NPs, first an aqueous solution of *p*(MVCA-*co*-St) was mixed with sodium tetrachloropalladate
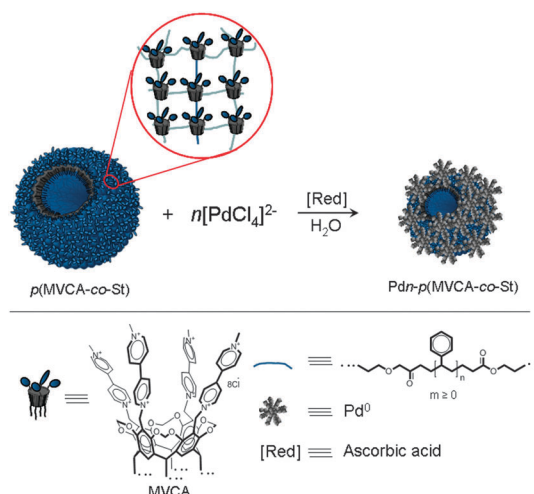
Scheme 1 Synthesis of Pd*n*-*p*(MVCA-*co*-St), *n* = 1–4.

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(1–4 equivalents in moles, relative to viologen-cavitand units) for the formation of $[PdCl_4]:MVCA$ complexes[15] and then ascorbic acid was added for the soft reduction of palladium ions (Scheme 1 and Table S1 in the ESI†). The colour of the solutions changed from yellow to dark grey, indicating the formation of metallic palladium. In the UV/Vis spectrum the disappearance of the absorption band of $[PdCl_4]^{2-}$ at 410 nm proves the complete reduction of palladium ions (Fig. S1 in the ESI†). Transmission electron microscopy (TEM) and the energy dispersive X-ray spectrum (EDX) data confirm the successful synthesis of Pd NPs (Fig. 1). The Pd NPs obtained were dialysed and the palladium content was determined by X-ray fluorescence (XRF) analysis. The concentration of palladium in the clusters is very close to the concentration of $[PdCl_4]^{2-}$ used in the synthesis, suggesting that all of the palladium is taken into the Pd NPs (see the ESI†). According to the TEM images the average size of the Pd NPs is about 5 nm, and they assembled into NP flower-like clusters (Fig. 1 and 2). The clusters are stable in water and can be stored at room temperature for more than three weeks without clouding and precipitation. Any significant changes in the TEM images

Fig. 1 (A and B) TEM images and (C) EDX profile of Pd4-*p*(MVCA-*co*-St); (D) TEM image of *p*(MVCA-*co*-St). The inset of B shows the close-up view of Pd4-*p*(MVCA-*co*-St).

Fig. 2 TEM images of Pd*n*-*p*(MVCA-*co*-St), *n* = 1 (A); 2 (B); 3 (C); 4 (D).

and UV/Vis spectra of the clusters were not observed, confirming the stability of the clusters (Fig. S1 and S2 in the ESI†). Evidently, *p*(MVCA-*co*-St) serves as a supporting matrix for the stabilization of Pd NPs and their association into a Pd NP cluster Pd*n*-*p*(MVCA-*co*-St, *n* = 1–4). In the ^1H NMR spectra of the clusters, the signals of *p*(MVCA-*co*-St) are dramatically broadened and could not be properly detected. It indicates that all the *p*(MVCA-*co*-St) molecules are involved in the building of clusters, and the Pd NPs are uniformly distributed on the polymeric shells (Fig. S3 in the ESI†).

p(MVCA-*co*-St) is a spherical network with viologen-cavitands as nodes and alkyl chains as links (Scheme 1). Usually, such porous spheres serve as a supporting matrix for the growth and stabilization of the MNPs in the cavity after the metal seeds pass through the pores.[24] However, in the case of *p*(MVCA-*co*-St), the Pd NPs are located on the surface of the network grouping in NP clusters (Scheme 1). This feature is caused by the ability of viologen groups to effectively stabilize MNPs, as it was shown previously for Pt NPs immobilized on the surface of viologen-micelles.[17]

As opposed to viologen-micelles, the shape of *p*(MVCA-*co*-St) is flexible and tunable, and therefore *p*(MVCA-*co*-St) can shrink, adapting to the Pd NP formation and to their association in the clusters. The cluster formation is caused by the tendency of MNPs to aggregate in aqueous solutions. In our case, the Pd NP aggregates do not precipitate from solution, they are stabilized on the polymeric shell *p*(MVCA-*co*-St). Moreover, the cluster aggregation of Pd NPs forces the *p*(MVCA-*co*-St) deformation.[25] As evident from the TEM images (Fig. 1 and 2, and Table S2 in the ESI†), the size of Pd*n*-*p*(MVCA-*co*-St) is much smaller than *p*(MVCA-*co*-St), suggesting the shrinkage of *p*(MVCA-*co*-St) in Pd*n*-*p*(MVCA-*co*-St). A similar pattern is observed by the dynamic light scattering (DLS) experiment: the hydrodynamic diameter of free *p*(MVCA-*co*-St) is found to be larger than the hydrodynamic size of the clusters (Fig. S4 and Table S2 in the ESI†).

All the clusters obtained have the same morphology but their size depends on the quantity of $[PdCl_4]^{2-}$ applied (Fig. 2, and Fig. S4 and Table S2 in the ESI†). Decrease in the amount of $[PdCl_4]^{2-}$ results in a decrease in the size of the clusters. Evidently, *p*(MVCA-*co*-St) shrinks more for a smaller amount of the Pd NPs to be clustered. The smallest hydrodynamic diameter is observed for Pd1-*p*(MVCA-*co*-St), which is almost 3.5 times less than that of the free *p*(MVCA-*co*-St) (Fig. S4 and Table S2 in the ESI†).

Using a larger amount of $[PdCl_4]^{2-}$ (more than 4 equivalents per cavitand) leads to the clouding of the solution, and after 24 hours, a grey precipitation appears. Obviously, 1:4 (MVCA unit:$[PdCl_4]^{2-}$) is an optimal ratio for the creation of a stable Pd NP cluster on the *p*(MVCA-*co*-St) matrix with a high density of metal on the surface.

The catalytic behaviour of the clusters was studied *via* the probe reduction reaction of *p*-nitrophenol. The reaction is widely used in the analysis of the catalytic activity of MNPs because it can be easily monitored by changes in the UV/Vis spectrum. The reduction of *p*-nitrophenol was carried out with an excess amount of sodium borohydride in water at 20 °C. The reaction does not occur in the absence of a catalyst, and it is activated by the addition of metals.[19–21]
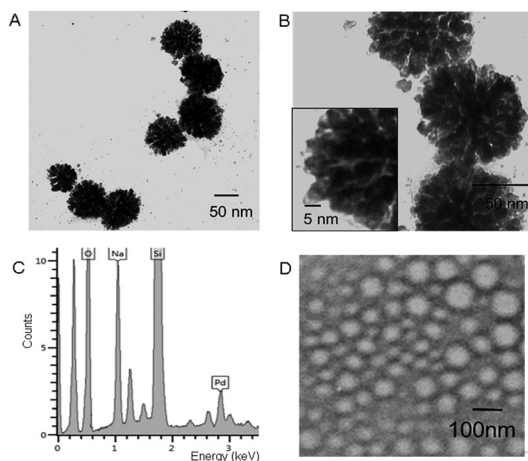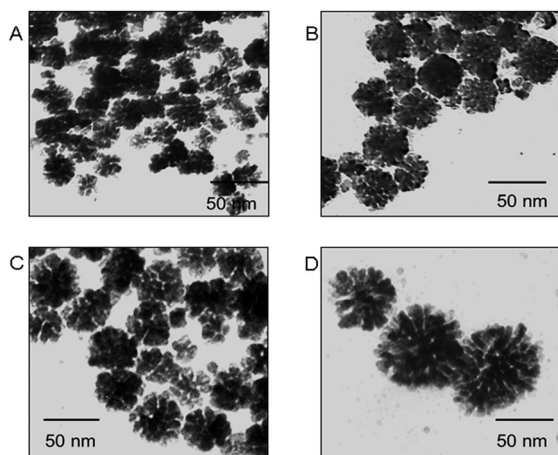
Table 1 Catalytic activity of the Pdn-p(MVCA-co-St), n = 1–4 clusters for the reduction of p-nitrophenol^a

Catalyst	Pd^0 (mole)	Apparent rate constant, k_{app} (s^{-1})	Normalized rate constant (mol^{-1} s^{-1})
Pd1-p(MVCA-co-St)	3.2×10^{-9}	0.0022	6.9×10^5
Pd2-p(MVCA-co-St)	3.2×10^{-9}	0.0022	6.9×10^5
Pd3-p(MVCA-co-St)	3.2×10^{-9}	0.0029	9.1×10^5
Pd4-p(MVCA-co-St)	3.2×10^{-9}	0.0027	8.5×10^5
Free Pd NPs^b	7.4×10^{-9}	0.00009	1.2×10^4

^{a} C(p-nitrophenol) = 0.1 mM, C(NaBH$_4$) = 5 mM, V = 1.62 ml, 20 °C, H$_2$O.
^{b} Were isolated from Pd4-p(MVCA-co-St) (see the ESI).

All synthesized clusters Pdn-p(MVCA-co-St) show a very high catalytic activity. 3.2 nanomoles (0.34 μg, Table S3 in the ESI†) of Pd in the clusters is sufficient to complete the reduction of p-nitrophenol (0.1 mM 1.6 ml) over ten minutes (Table 1 and Fig. 3). The amount of Pd applied is hundred times less than that usually used in catalysis. In the literature, we have found only one article about such an effective catalyst in the reduction of p-nitrophenol.[10] Prof. T. Kawai *et al.* reported on highly active Pd and Pd–Ni nanowires which contain associated MNPs similar to the Pdn-p(MVCA-co-St). Considering their own data and previous studies,[26,27] the authors assume that the reason behind such a high catalytic activity is the presence of disordered metal atoms in aggregated domains.

Fig. 3 illustrates the temporal changes in the UV/Vis spectra of a mixture of sodium borohydride and p-nitrophenol after the addition of Pd4-p(MVCA-co-St). An absorption band of p-nitrophenol at 400 nm decreases and an absorption peak of p-aminophenol appears at 300 nm. The reduction is a pseudo-first-order reaction due to the 50-fold excess of Na$_2$BH$_4$ used. A linear correlation between $\ln(C_t/C_0)$ and the reduction time is observed from 250 seconds after the initial induction period[19] (Fig. 3B and Fig. S5 in the ESI†). In Table 1 the apparent rate constants k_{app} and the activity of the synthesized clusters are shown. From the above kinetic data it can be concluded that all the clusters Pdn-p(MVCA-co-St) have a similar catalytic activity, which depends only on the amount of Pd. The ratio Pd : MVCA in the clusters does not significantly affect the catalytic properties.

So, p(MVCA-co-St) neither improves nor worsens the activity of the Pd NPs; it only contributes to their stabilization

Table 2 Suzuki–Miyaura coupling reaction catalyzed by Pd4-p(MVCA-co-St)^a

Catalyst	Pd^0 (mol%)	Time (h)	Solvent	T (°C)	Yield (%)
Pd4-p(MVCA-co-St)	0.5	40	H$_2$O	r.t.	86
Pd4-p(MVCA-co-St)	1	40	H$_2$O	r.t.	∼98

^{a} C(iodobenzene) = C(phenylboronic acid) = 5 mM, C(K$_2$CO$_3$) = 15 mM, V = 15 ml.

and assemblies. Nevertheless, the "pure" Pd NPs extracted from Pd4-p(MVCA-co-St) by centrifugation (see the ESI†) demonstrate an inferior catalytic activity in comparison with the Pdn-p(MVCA-co-St) (Fig. 3B and Table 1).

Palladium nanoparticles are commonly tested in the Suzuki–Miyaura coupling reaction, which is one of the most practiced reactions of C–C bond formation. We carried out the Suzuki–Miyaura reaction in water at room temperature in the presence of 0.5–1 mol% of the Pd4-p(MVCA-co-St). Under such mild conditions, we succeeded in obtaining milligrams of biphenyl in good yields (86–98%) (Table 2). Stirring the dispersion containing iodobenzene, phenylboronic acid, potassium carbonate and 0.5 mol% of Pd in Pd4-p(MVCA-co-St) for 40 hours resulted in the formation of 10 mg (86%) of biphenyl. The reaction yield reached nearly 98% with 1 mol% of the catalyst (Table 2). The product was isolated by extraction with hexane. Its ^{1}H NMR spectrum is shown in Fig. S6 in the ESI.†

In conclusion, we have described a simple method for the synthesis of the nanosized Pd NP clusters with high catalytic activity. A flexible network p(MVCA-co-St) was used as a supporting matrix. p(MVCA-co-St) stabilizes Pd NPs in water and adapts to the Pd NP cluster formation. One to four equivalents of the Pd (relative to MVCA units) can be introduced into the clusters of size ranging from 30 to 80 nm. The synthesized Pd NP clusters are stable in water and do not precipitate for a long time. Their highly effective catalytic properties are demonstrated in the reduction reaction of p-nitrophenol and in the Suzuki–Miyaura coupling reaction carried out in water at room temperature.

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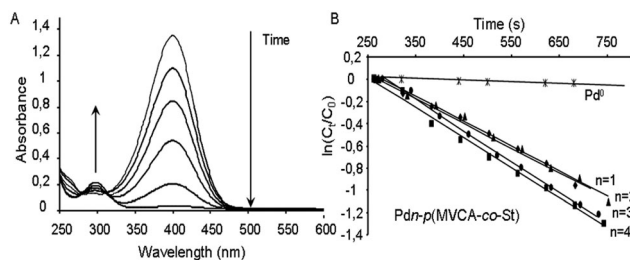9 G. W. Qin, W. Pei, X. Ma, X. Xu, Y. Ren, W. Sun and L. Zuo, *J. Phys. Chem. C*, 2010, **114**, 6909–6913.

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